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(21) International Application Number: PCT/US97/08465 (22) International Filing Date: 19 May 1997 (19.05.97) (30) Priority Data: 60/018,637 30 May 1996 (30.05.96) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MOSS, Philip, Osborne [US/US]; 205 Wellington Road, Wilmington, DE 19803 (US). SWEVAL, Charles, Robert, Jr. [US/US]; 3121 Wellborne Drive West, Mobile, AL 36695 (US). (74) Agent: GREGORY, Theodore, C.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: AN IMPROVED PROCESS FOR PREPARING ANHYDROUS HCN (57) Abstract <p>This invention relates to a batch or continuous process for the preparation of anhydrous HCN comprising reacting alkali metal or alkaline-earth metal salts of cyanide with mineral acids in a reactor followed by transfer to a fractionating column and results in low polymer formation and high product yield.</p>		

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TITLEAN IMPROVED PROCESS FOR PREPARING ANHYDROUS HCNFIELD OF THE INVENTION

5 This invention relates to a process for producing anhydrous hydrogen cyanide and more particularly to a batch or continuous process for producing anhydrous hydrogen cyanide from sodium cyanide and sulfuric acid.

BACKGROUND OF THE INVENTION

10 A laboratory method for preparing HCN from NaCN and sulfuric acid followed by batch distillation using a reactor/still vessel can be found in The Handbook of Preparative Inorganic Chemistry 1965, p. 658. In the above handbook disclosure, the HCN was made anhydrous by removal of the water fraction in the vapor stream by absorption in concentrated sulfuric acid rather than by distillation.

15 There is a need for a convenient way to prepare anhydrous HCN economically in quantities lower than could be justified by large standard commercial methods such as the Andrussow process which uses ammonia, methane and catalyst at high temperature. Such a process becomes increasingly attractive for small quantity HCN users as commercial manufacturers of HCN become more reluctant to ship the material in any kind of container. The process invented here provides such needs and also permits production of the anhydrous HCN as needed for direct use in commercial processes (eg. pesticides, pharmaceuticals) and
20 substantially lowers the amount of on-site storage of the product.

SUMMARY OF THE INVENTION

25 A batch or continuous process has been discovered for the preparation of anhydrous HCN by reacting alkali metal or alkaline-earth metal salts of cyanide with mineral acids in a solvent at a temperature of from 10 to 60°C and a pH from 0 to 4 to form a reaction product comprising HCN in solution, transferring the liquid reaction product to a fractional distillation column and recovering the anhydrous hydrogen cyanide from the fractionating column. This process results in low polymer formation and high product yield.

DETAILS OF THE INVENTION

30 The batch and continuous processes of the invention have been developed to offer safe, practical methods of producing anhydrous HCN from its sodium salt and results in low polymer formation and high chemical yield on a scale of .05-5MM lb/yr. The low polymer formation is key to being able to achieve practical, commercial scale fractional distillation of the resulting aqueous solution in high yield. The following reaction conditions further define the invention.

35 The process of the invention can be carried out batchwise or continuously. In the batch mode, all the acid can be charged first, or it can be co-fed with the cyanide salt solution. The pH should be acidic throughout the reaction from pH 0 to 4 preferably below 3 to prevent HCN polymer formation. In carrying out the continuous process, the cyanide salt solution

and acid are co-fed in the mole ratio described herein to a reactor with agitation. The discharge from the reactor is controlled by its level. Since the reaction is immediate in both the batch and continuous process, from a practical standpoint, there is no upper or lower residence time on this reactor.

5 In the process of the invention, the only known suitable solvents are water or an aqueous reaction product recycled from the fractionating column which is typically present at between about 50-99% by weight water. The reaction temperature should be maintained between 10 and 60°C, with the preferred temperature range between 20 and 40°C to minimize HCN hydrolysis, and to maintain solubility of the HCN and salt by-products in the
10 reaction mass.

The mineral acids of the invention are sulfuric and phosphoric. However, sulfuric acid is preferred for economy and environmental reasons. Before feeding into the reactor, the mineral acid is diluted below 90% with water, or the recycled reaction product from the bottom of the distillation column. Preferably, the sulfuric or phosphoric acid concentration is
15 25-45% on a salt-free basis or 15-35% including the salts in the recycled reaction product from the bottom of the distillation column. A lower concentration can be used, but aqueous waste increases and the batch reactor and the distillation column become larger as a result of higher dilution. Somewhat higher concentrations can be tolerated, up to 70%, but increased yield loss to formate results. It may be necessary to add NaOH to stabilize aqueous NaCN.
20 Anyone skilled in the art would know the amount of NaOH to add. For reasons of safety and economy the dilution of the mineral acid is preferably below a concentration of 50% with the water or the stripped salt solution recycled from the bottom of the fractionating column. The major consideration here is the amount of water to be introduced to the reactor. There must be sufficient water to prevent large amounts of the by-product salts from precipitating
25 out of solution during the reaction and prior to distillation.

Alkali metal and alkaline-earth metal salts of cyanide can be used, however, the preferred salt is sodium cyanide for reasons of availability and economy. The cyanide salt should be dissolved completely in water before introduction into the reaction process.

The mole ratio of cyanide salt to acid is related to the number of available acidic
30 protons. In theory there are two available protons for (H₂SO₄) and three available protons for (H₃PO₄). For example, the mole ratio of salt (NaCN) to acid (H₂SO₄) is less than 2 and the mole ratio of salt (NaCN) to (H₃PO₄) is less than 3. Using the preferred salt (NaCN) and acid (H₂SO₄), the preferred mole ratio should be between 1.5 and 1.85 for environmental reasons, economy and safety. The preferred mole ratio for NaCN and H₃PO₄ should be
35 between 2.5 and 2.85.

The cyanide is added to the acidic reactor employing typical techniques that ensure good micro-mixing at the addition point. It is important to minimize the time that the hydrogen cyanide might "see" a pH of above 4 to minimize HCN polymer formation.

Addition time is not important and is only limited by the capacity of the equipment to remove the heat generated by the reaction. The reaction occurs immediately at all temperatures outlined above.

The water/HCN/salt reaction product feed to the fractionating column must be low in HCN polymer for the purpose of reliability. A dark (high polymer) reaction product will lead to fouling and pluggage of the column that will require clean-out more often. Typically the HCN concentration in the reactor before transfer to the fractionating column is 1-10% preferably 3-7%. Higher concentrations of HCN can lead to increased vaporization loss and polymer formation at the operating temperatures.

Preferred is the process wherein anhydrous HCN is prepared in a batch or continuous process by reacting sodium cyanide with sulfuric acid in a reactor where the solvent is water, the reaction temperature range is between 20 and 40 °C, the mole ratio of sodium cyanide to sulfuric acid is between 1.5 and 1.85, the cyanide is added employing good micro-mixing techniques followed by transferring the water/HCN/salt reaction product to a fractionating column and separating the desired anhydrous HCN. What is meant by anhydrous HCN is at least 98.5% HCN.

The process of the invention produces less HCN polymer and results in less hydrolysis of the HCN and is therefore superior to processes known presently.

The process of this invention can be further illustrated by the following examples. In the examples the slightly yellow tinted solution indicates low HCN polymer content.

EXAMPLE 1

Preparation of HCN - Batch Process

To a one liter resin kettle reactor equipped with mechanical stirring were charged 153.5 g 98% H_2SO_4 and 382.0 g water. In a separate vessel, 126 g of 99% NaCN were totally dissolved in 495.4 g water and 5.0 g 50% NaOH at room temperature. Using a 250 ml reservoir and a low flow charging pump, the NaCN solution was charged to the reactor subsurface over the period of one hour while maintaining the reactor temperature at 25 °C. The resulting water/salt/HCN slightly yellow tinted solution was fractionally distilled by feeding to the middle of a 20 plate jacketed Oldershaw column equipped with an electrically heated round bottom flask reboiler with discharge pump, refrigerated glycol cooled condenser and timed distillate reflux controller and round bottom distillate receiver. HCN distillate obtained: 57.3 g, 83.2% crude yield, water content 0.06%. HCN yield from cyanide mass balance in liquid streams: 86.9%. Chemical yield loss to measurable by-products in liquid streams (formate): <1.0%.

EXAMPLE 2

Preparation of HCN - Batch Process

A series of six batch reactions were carried out in a jacketed, mechanically agitated, 3000 gallon (11,350 liter) glass lined steel reactor. The reactor was equipped with an

external circulating cooler loop and feed lines for aqueous sodium cyanide, sulfuric acid, and water/recycle brine from the previous distillation batch. Provisions were included to allow premixing and cooling in-line of the sulfuric acid and water/recycle brine streams while charging the reactor. The reactor was inerted and vented to an aqueous scrubber.

- 5 The 66 degree Baume (93.7%) sulfuric acid charge of 2970 lb (1348 Kg) was mixed in-line with 9735 lb (4420 Kg) of recycle brine (20-25 wt % salts) and cooled in line to 35 °C while feeding the reactor over 70 to 80 minutes. With agitation, and cooling via the reactor jacket, 15,397 lb (6990 Kg) of prechilled (15 °C) 14.3 wt % aqueous sodium cyanide was metered in over 80 to 90 minutes while maintaining the reactor temperature at 35 °C.
- 10 The sodium cyanide feed was introduced subsurface near the agitator to ensure good mixing with an endpoint pH of less than 3.0.

- The resulting 4.3wt% HCN slightly yellow aqueous brine mixture was then fed to the middle of a packed glass lined fractional distillation column equipped with a steam-heated reboiler, refrigerated brine condenser, and a reflux accumulator with reflux feed controls.
- 15 Distillate hydrogen cyanide was fed directly to the user. Approximately 30 to 40% of the stripped bottoms brine was accumulated and recycled for sulfuric acid dilution in the next batch. HCN crude yield basis distillate (6 batch ave.): 91.9%, 1115 lb, 507 kg, bp 26-27 °C. HCN yield basis complete cyanide balance on all liquid streams including hold-ups and distillation bottoms, (6 batch ave.): 99.6% (1208 lb, 549 kg). Average HCN yield loss to by-
- 20 products (formate) 0.4%. Yield loss to distillation in bottoms is 2.4 to 6.0%, 5.5% average and varies with the particular experimental equipment used.

EXAMPLE 3

Preparation of HCN - Continuous Process

- An apparatus consisting of a reaction and distillation system in series was set up. The
- 25 reaction system was made up of a 1 liter resin flask, with cooling, mechanical stirring, two charging reservoirs with their accompanying charging metering pumps feeding to the reactor subsurface, dry ice condenser, and a reactor discharge metering pump for transfer to the distillation system. The distillation system consisted of a 20 plate Oldershaw column, round bottom flask reboiler with discharge pump, timed distillate reflux control, refrigerated glycol
- 30 cooled condenser, and distillate receiver. Both the reactor and distillation systems were vented to a common aqueous scrubber.

- The reactor and distillation column reboiler each were charged with 256.4 g of a 2.5% H₂SO₄ solution. In separate flasks, reactant solutions were made up: 1) NaCN solution consisted of 281.3 g 99% NaCN, 1114.7 g water and 11.3 g 50% NaOH, and 2) a 43%
- 35 sulfuric acid solution consisted of 331.2 g 98% H₂SO₄ and 423.8 g water. The NaCN solution and the 43% sulfuric acid solution were partially charged separately to the two charging reservoirs which were then started simultaneously, maintaining even flows and a reactant mole ratio of 1.7 moles cyanide per mole sulfuric acid over a period of about 4 hrs.

Both additions were made subsurface near the agitator for good mixing. Cooling was applied to the reactor as needed to maintain the 50 °C temperature. The reactor charging reservoirs were replenished with solutions as needed until they were consumed. A volume of approximately 250 ml was maintained in the reactor and the slightly yellow tinted reactor discharge was pumped to the midpoint of the distillation column and distilled in a continuous manner. The distillate was collected in two fractions. The HCN distillate obtained: 1st cut 41.3 g HCN, .205% water, 2nd cut 69.2 g HCN, 1.33% water. Total: 110.5 g distillate. Crude yield: 71.2% HCN. Yield calculated from cyanide balance of liquid streams: 74.6% HCN. Chemical yield loss from measurable by-products in liquid streams (formate): < 1.0%

EXAMPLE 4

Preparation of HCN - Batch Process

A series of 20 batch reactions were carried out in the reactor and distillation equipment as described in Example 2.

The reaction and distillation systems were water flushed after each batch, and this flush (average 3259 lb; 1480 kg) was returned to the reactor. To the flush the following charges were made; a) 3030 lb (1375 kg) average of 93% sulfuric acid co-fed with 9465 lb (4297 kg) average recycle brine cooled in-line as previously described; b) 13144 lb (5967 kg) average of 17 wt% prechilled aqueous sodium cyanide metered as previously described while maintaining the 35 degree C reaction temperature, with an endpoint pH of less than 3.0.

The resulting 4.3 wt% HCN slightly yellow aqueous brine was then distilled as previously described with 30 to 40% of the stripped bottoms brine recycled into the next batch for sulfuric acid dilution.

CLAIMS

What is claimed is:

1. A process for the batch or continuous production of anhydrous hydrogen cyanide comprising reacting an alkali metal or alkaline metal salt of cyanide with a mineral acid in the presence of a solvent at a temperature of 10 to 60°C, a pH of 0 to 4, said cyanide salt, mineral acid being present at a mole ratio of less than 3:1 of cyanide to acid to form hydrogen cyanide in a reaction product, transferring the reaction product to a fractional distillation column and recovering anhydrous hydrogen cyanide from the fractionating column.

2. A process of Claim 1 wherein the mineral acid is sulfuric acid and the ratio of sodium cyanide to acid is less than 2:1.

3. The process of Claim 1 wherein the solvent is aqueous reaction product from the bottom of the distillation column.

4. The process of Claim 3 wherein ratio of cyanide to acid is 1.5:1 to 1.85:1.

5. The process of Claim 1 wherein the solvent is water.

6. The process of Claim 1 wherein the mineral acid is phosphoric acid and the ratio of sodium cyanide to acid is 2.5:1 to 2.85:1.

7. The process of Claim 1 wherein the temperature is 20-40°C.

8. The process of Claim 1 wherein production of anhydrous cyanide is by a continuous process.

9. The process of Claim 8 wherein the mineral acid is sulfuric acid and the temperature is 20-40°C.

10. The process of Claim 1 wherein the production of anhydrous hydrogen cyanide is a batch process.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/08465

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01C3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 160 413 A (ALLISON JOE D) 3 November 1992 see column 5, line 1 - line 12; claims ---	1-7,9,10
X	US 1 347 518 A (MUELLER) 27 July 1920 see page 2, line 17 - line 33; figure ---	1-5,7-9
X	GB 599 606 A (AMERICAN CYANAMID) 17 March 1948 see the whole document ---	1-10
A	US 1 352 655 A (BUCHANAN) 14 September 1920 see page 2, line 18 - line 33 ---	2,4,6
A	US 1 680 662 A (BROWN) 14 August 1928 see page 3, line 1 - line 39; figure -----	1,5,7,10

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5160413 A	03-11-92	NONE	
US 1347518 A	27-07-20	NONE	
GB 599606 A		NONE	
US 1352655 A	14-09-20	NONE	
US 1680662 A	14-08-28	NONE	